

FINAL REPORT

**NON-VOLATILE PRECURSORS TO
ALTERNATIVE HALON FIRE EXTINGUISHING AGENTS**

AFOSR Grant Number: F49620-94-1-0270

Principal Investigator: William W. Bannister
Department of Chemistry
University of Massachusetts/Lowell
Lowell, Massachusetts 01854

Program Managers:
Dr. Frederick Hedberg and Dr. Walter Kozumbo
Air Force Office of Scientific Research
Bolling AFB, D.C.

31 October 1997

(Resubmitted: 28 July 2000)

20000908 047

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-00-

Public reporting burden for this collection of information is estimated to average 1 hour per response gathering and maintaining the data needed, and completing and reviewing the collection of information, including suggestions for reducing this burden, to Washington Headquarters: Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget.

ata sources,
spect of this
15 Jefferson
503.

1. AGENCY USE ONLY (Leave blank)			2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
			31 October 1997	Final - 1 May 1994 - 31 August 1997
4. TITLE AND SUBTITLE			5. FUNDING NUMBERS	
Non-Volatile Precursors to Alternative Halon Fire Extinguishing Agents			F49620-94-1-0270	
6. AUTHOR(S)			8. PERFORMING ORGANIZATION REPORT NUMBER	
William W. Bannister Department of Chemistry				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)			9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	
University of Massachusetts/Lowell Lowell, Massachusetts 01854			AFOSR/NL 801 North Randolph Street Arlington, VA 22203-1977	
11. SUPPLEMENTARY NOTES			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
12a. DISTRIBUTION AVAILABILITY STATEMENT			12b. DISTRIBUTION CODE	
APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED				
13. ABSTRACT (Maximum 200 words)				
NVP agents have greatly reduced ODP, GWP and toxic vapor properties, and pose greatly reduced atmospheric emissions due to fire extinguishing operations or from accidental releases. Agent requirements for firefighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances. This improved agent system may be beneficial in terms of optimizing usage of Halon streaming agents in the Halon Bank. NVP agents can be incorporated into fire preventive paints and resins which will release Halon agents upon exposure to high heat.				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
Halon, extinguising, fire			24	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	
Unclassified	Unclassified	Unclassified		

CONTENTS

	Page
ABSTRACT	1
BACKGROUND	1
SUMMARY OF RESEARCH EFFORTS	3
Chemical modifications	4
Addition polymerizations	4
Comments on polyolefins	5
Halogenated polyesters	8
Polyesters derived from 2,2,3,3-tetrabromo-1,4-butanediol	8
Cellulose Tribromoacetate	10
Polyvinyl Tribromoacetate	10
Physical modification (gelation) of high volatility Halons	13
Amine gelling agents ...	13
Hydrophobic fumed silica gel formulations	15
HypOITM prepolymer gels	15
PROBLEM AREAS	15
RECOMMENDATIONS FOR FUTURE WORK	16
SIGNIFICANCE OF RESULTS	20
PERSONNEL SUPPORTED	20
PUBLICATIONS	20
INTERACTIONS	21
NEW DISCOVERIES, INVENTIONS, PATENT DISCLOSURES	21
HONORS/AWARDS	21
REFERENCES	21
ACKNOWLEDGEMENTS	22

LIST OF FIGURES

Figure 1. Pyrolysis of Poly(dibromoethylene) (“PDBE”)	5
Figure 2. Pyrolysis of Polybromotrifluoroethylene) (“PBTFE”)	6
Figure 3. Postulated reaction coordinate diagram for PBTFE	7
Figure 4. TGA of Poly(2,2,3,3-tetrabromo-1,4-butyleneoxalate)	10
Figure 5. TGA of Cellulose Tribromoacetate	11
Figure 6. TGA of Polyvinyl Pyrolysis of Tribromoacetate	12
Figure 7. Modified flame thrower for projection of gelled Halon formulation	14
Figure 8. Hyperbranched polyglycerol, prepared in one step	16

LOW VOLATILITY HALON FIRE EXTINGUISHING AGENTS WITH REDUCED GLOBAL ENVIRONMENTAL IMPACTS

ABSTRACT

The continuation of work on non-volatile precursors (NVPs), which pyrolyze in the heat of a fire to generate Halon-like fire extinguishing agents, will be discussed. Both chemical and physical modifications of existing Halon or Halon alternative agents are being studied. From the chemical standpoint, syntheses of new polyolefinic fluorobromocarbons and brominated polyolefins polyesters have been attempted. One of these (polyfluorotribromoethylene, PFTBE) appears particularly promising, and investigations are being pursued on several other candidates.

In terms of physical modifications, high volatility conventional and alternative Halons can also be gelled using a variety of highly effective gelants to form relatively nonvolatile formulations.

NVP agents have greatly reduced ODP, GWP and toxic vapor properties, and pose greatly reduced atmospheric emissions due to fire extinguishing operations or from accidental releases. Agent requirements for firefighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances.

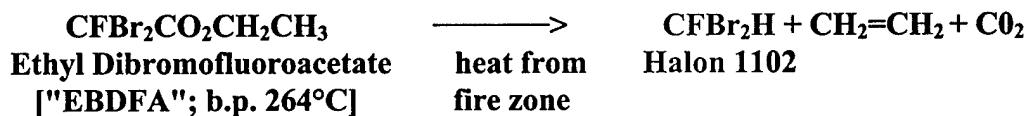
Moreover, since much less of these agents would be required for adequate extinguishment (due to the low volatility and loss due to evaporation en route to the fire) these would appear to be actually even more effective than the conventional Halons.

This work concerns innovative non-volatile precursor (NVP) agents which generate highly effective hydrobromofluorocarbon (HBFC) and olefinic bromofluorocarbon fire extinguishing agents when heated at temperatures as would be encountered in typical fire zones. Initial research has shown that some of these NVP agents are as effective as the most efficient Halon agents now in use. This work is relevant because the Halons are being phased out due to their impact on the stratospheric ozone layer. The objective of this work was to attempt to find acceptable Halon alternative agents.

BACKGROUND

Within the past few years there has been much attention directed to possible drop-in replacements for Halon fire extinguishing agents which are now no longer in production, due to their unacceptable ozone depletion and global warming potentials IODP, GWP]. Large stockpiles of Halons 1211 (CF_2BrCl ; b.p. -2.5°C), 1301 (CF_3Br , b.p. -58°C), and to a lesser extent 2402 ($\text{CF}_2\text{BrCF}_2\text{Br}$, b.p. 47°C) are still maintained in the Halon bank, however, for future use on a prioritized basis for firefighting requirements. For total flood agent systems, one of the most promising high volatility candidates is trifluoromethyl iodide (CF_3I , b.p. = -22°C). For streaming and similar agent compositions requiring lower volatilities, a variety of fluorocarbon (e.g., C_6F_{14} b.p. 60°C) and hydrochlorofluorocarbon (e.g., HCFC 123 (CF_3CHCl_2 b.p. = 27°C)) compositions have been tested and mark. For streaming agent applications even the higher boiling of these compositions are still sufficiently volatile that very large amounts of such agents need to be delivered to a fire in order to ensure adequate extinguishing concentrations; most of the agent is lost in delivery to the fire zone. None of these agents enjoys the low toxicities provided by the Halons; and, particularly for the HCFC agent systems, moderate but probably eventually unacceptable ODP and GWP parameters pertain.

Since the poor deliverability and requirements for excessive dose delivery, and the high ODP, GWP and vapor toxicity problems are all due to the moderate to high volatilities of these compounds, we initiated an investigation of non-volatile precursor (NVP) fire-fighting agents which would degrade in the heat of fire to release analogs of conventional Halons. The first phase of project work, completed two years ago, involved the synthesis and study of several new compounds which decompose thermally to yield olefins and hydrobromofluorocarbon (OBFC, HBFC) products. One early example of such NVPs was ethyl dibromofluoroacetate (EBDFA) which decomposes to Halon 1102:



The compounds were tested for fire extinguishing efficiency at the US Air Force Wright Laboratories Fire Research Division at Tyndall Air Force Base, Florida [TAFB]. All of the compounds had good cup burner extinguishing values; two of the agents (including "EBDA", above) were actually superior in fire extinguishing performance to the Halons.

The compounds which were initially investigated were all liquid species of fairly simple molecular structure. The entire thrust of this study was to ascertain the general feasibility of thermal cracking of large molecules to afford gaseous Halon-like extinguishing agents in the heat of a fire. Although no toxicity studies were performed, it was understood that all of the initial agents would be unacceptably toxic, particularly in terms of ingestion or absorption through the skin. Having

demonstrated, however, the general feasibility of this approach, attention was directed in the current research program to development of NVP fire extinguishing agents which would be safe, cheap and efficient. Such NVP agents would have greatly reduced ODP, GWP and toxic vapor properties, and would pose greatly reduced atmospheric emissions due to fire extinguishing operations or from accidental releases. Agent requirements for firefighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances. This improved agent system may be beneficial in terms of optimizing usage of Halon streaming agents in the Halon Bank.

The most advantageous solid materials were decided to be synthetic condensation polymers. These materials do not require high molecular weights and have the repeat units that would effectively imitate the thermal behavior of the simple molecular compounds of the early studies. In particular, polymers that would decompose thermally by an "unzipping" mechanism would produce small molecules capable of fire extinguishment. Many of these materials decompose cleanly and produce no significant char or other residues. We therefore looked at the thermal properties of these materials to develop reasonable screening criteria for these materials, and concluded that thermal gravimetric analysis (TGA) would be an excellent method of determining the feasibility of candidates for further testing.

SUMMARY OF RESEARCH EFFORTS

Two approaches were adopted in this study:

1. Chemical modifications of existing Halon or Halon alternative agents were studied. From the chemical standpoint, syntheses of new polyolefinic bromo- and fluorobromocarbons and of similar polyesters, were attempted.

One of these, poly(fluorotribromoethylene) [PFTBE] appears particularly promising, and further investigations will be recommended for applications of this agent. Three other candidates will also be recommended for further testing after determining that their potential extinguishing performances were similar to that of PTFE. These new agents are: poly(2,2,3,3-tetrabromo-1,4-butylene oxalate); cellulose tribromoacetate; and poly(vinyl tribromoacetate).

2. Physical modifications of existing high volatility Halons or alternatives were also studied. These include gelation (using a variety of highly effective gelants to form relatively non-volatile formulations); and encapsulation under pressure in expandable polymeric microspheres for delivery to a fire. The gelled systems appeared to be particularly attractive approaches for NVP agent development, and recommendations will be made for further attention to this line of approach.

CHEMICALLY DERIVED POLYMERIC NVP AGENTS

A. Addition polymerizations and reactions.

Radiation induced free radical initiation conditions were attempted, involving gamma radiation (0.1; 0.5; 1.0; and 2.0 megarad doses) in the UMASS-Lowell nuclear reactor; and aqueous emulsification free radical polymerizations were performed with surfactant and lauroyl peroxide initiation.

None of the gamma irradiation experiments were successful; all of these resulted in extensive debromination. No further gamma irradiation experiments are now contemplated, for this reason. As noted below, free radical emulsion polymerizations of three monomers were observed; others (polyvinyl bromide, and polybromotrifluoroethylene) were purchased.

<u>Monomer</u>	<u>Resulting Polymer</u>
Br-CH=CH-Br	(CHBr-CHBr) _n Poly(1,2-dibromoethylene); "PDBE" (see comments below)
CH ₂ =CBr ₂	(CH ₂ -CBr ₂) _n Poly(vinylidene bromide) (gummy, intractable polymer)
CH ₂ =CH-Br	(CH ₂ -CHBr) _n Poly(vinyl bromide) (submitted to Wright Labs, WPAFB for engine nacelle fire suppression evaluation)
CF ₂ =CFBr	(CF ₂ -CFBr) _n polybromotrifluoroethylene; "PBTFE" (see comments below; (submitted to Wright Labs, WPAFB for engine nacelle fire suppression evaluation))
CBr ₂ =CF ₂	NO POLYMERIZATION
CH ₂ =C(Br)-CF ₃	NO POLYMERIZATION
CHF=CBr ₂	NO POLYMERIZATION

Comments on Polyolefins

Of the four polymers which were obtained, polyvinylidene bromide proved too intractable as a gummy polymer for further work in this form. Our entire lot of poly(vinylbromide) was submitted for evaluation to Wright Laboratories for evaluation in engine nacelle fire suppression tests, although it was not anticipated to be a highly effective extinguishing agent in view of its low bromine content.

Thermal gravimetric analysis (TGA) was performed on poly(dibromoethylene) (PDBE) to ascertain extent and character of thermal depolymerization. As can be seen in Figure 1, this nonfluorinated polymer did not pyrolyze cleanly at all, and a large amount of char remained at the end of the cracking process; there appear to be a large number of independent cracking processes with no probability for a completely irreversibility.

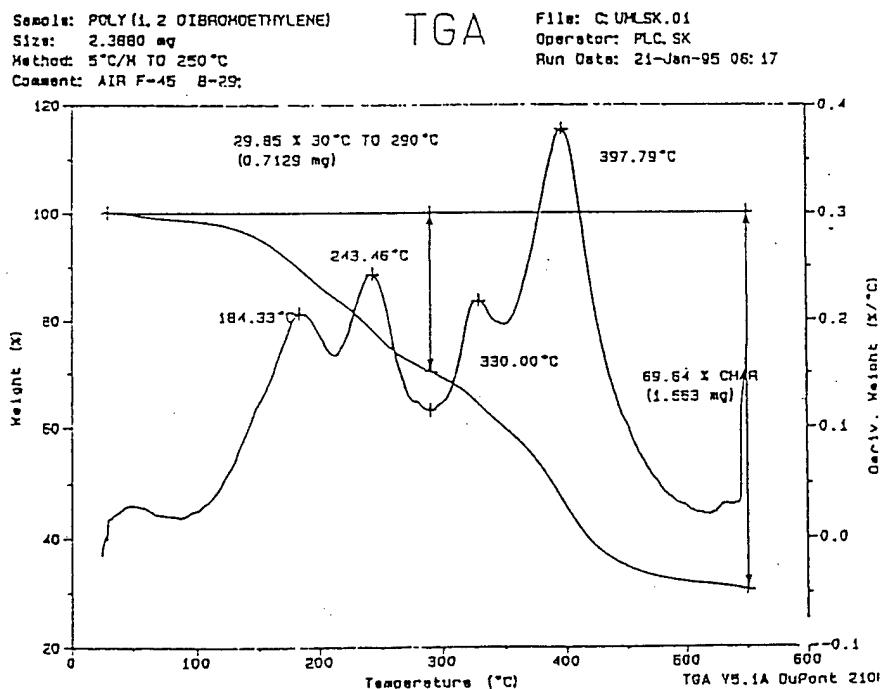
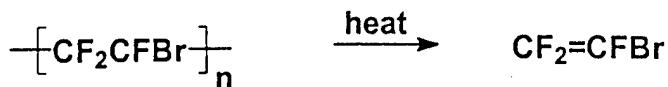


Figure 1. Pyrolysis of Poly(dibromoethylene) ("PDBE")

Based on TGA testing, polybromotrifluoroethylene (PBTFE), was selected as a promising for possible large scale fire testing in this fashion, since it appeared to decompose cleanly to bromotrifluoroethylene (BTFE):



PBTFE

BTFE; FC #1113B1

(BTFE, and several similar halogenated olefins were shown in work performed at Tyndall AFB to have cup burner extinguishing values similar to those of the conventional Halons.)

The TGA curve for PBTFE, shown in Figure 2, shows that cracking is essentially complete (with no significant char or other residue) 300° C, and with a relatively sharp thermal transition. A small amount of decomposition is observed at 150° C, due to small amounts of water present in the sample (water vapor was observed in the infrared spectrum). The cracking product was identified as the monomeric bromotrifluoroethylene building block, on the basis of the infrared spectrum. These conditions indicate reasonably high shelf stability at ambient temperatures and an ability to degrade at low fire temperatures.

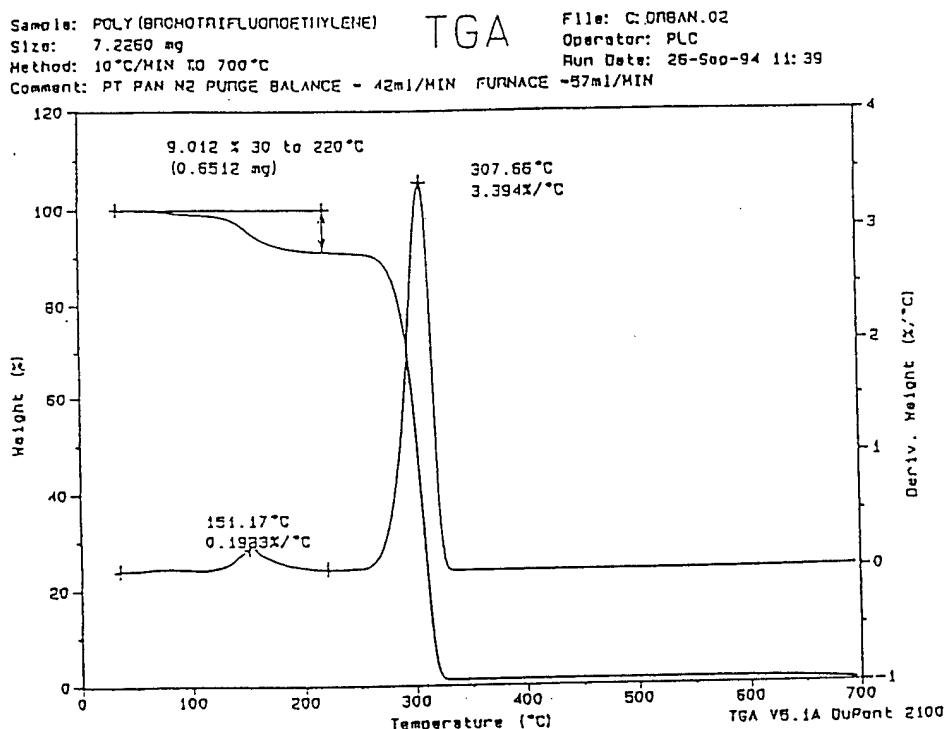


Figure 2. Pyrolysis of Polybromotrifluoroethylene (PBTFE)

It appears probable that the facile thermal degradation of the fluorinated poly(trifluorobromoethylene) ("PTFBE") can be attributed to a low energy of activation for a readily reversible polymerization process. It is known that the monomeric bromotrifluoroethylene can spontaneously polymerize under certain (proprietary; PCR Inc.) conditions, indicating a low energy of activation for this process. The retropolymerization should share the same energy of activation; hence the ease of depolymerization. It is then tempting to speculate that fluorine substitution facilitates cracking processes in general; see Figure 3. This would substantiate an earlier observation by Dr. Robert Tapscott at NMERI that fluoro groups are beneficial in fire extinguishing compositions.

We investigated synthetic methods for large scale preparation of PBTFE for field testing at Tyndall AFB, but attempts to prepared more of this polymer were unsuccessful, since the proprietary techniques for this were not available to this group, and PCR had ceased production.

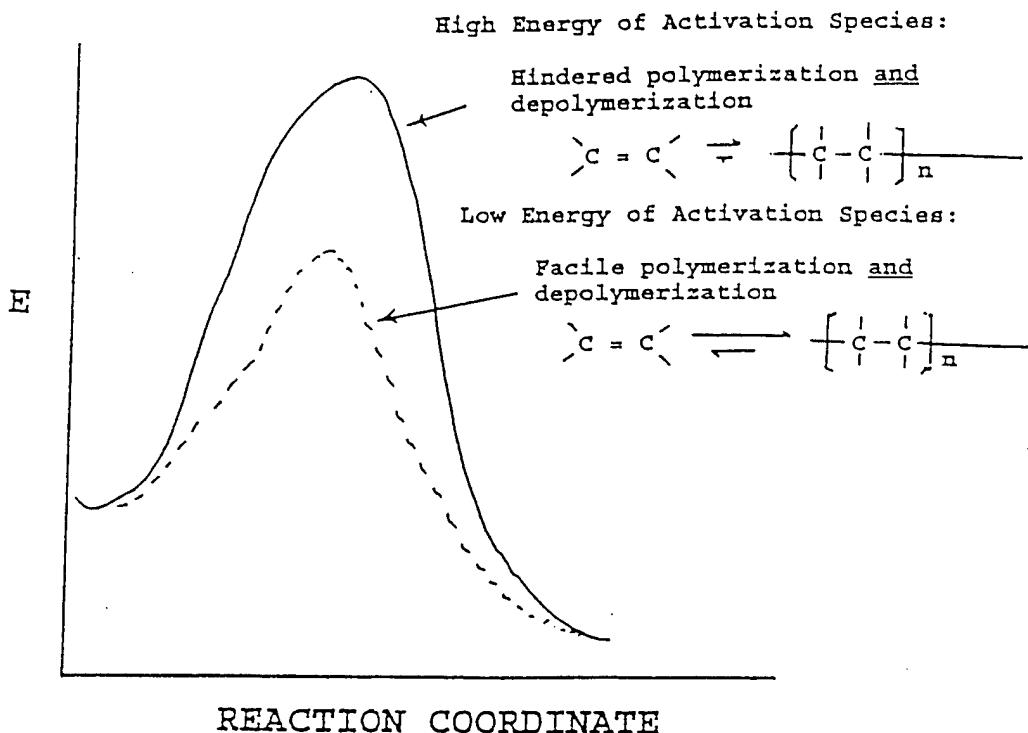


Figure 3. Postulated reaction coordinate diagram for PBTFE.

From the standpoint of determination of fire extinguishing capabilities, no good analog of the cup burner testing apparatus developed at NMERI and elsewhere exists for solid NVP agents. The monomeric bromotrifluoroethylene which was identified as being the sole product of cracking of PBTFE was tested using the NMERI cup burner apparatus at Tyndall AFB, with a value of about 5.5 being observed (as compared with values of about 3 for the Halons and for CF_3I ; and about 5.5 for HCFC 125).

In preliminary "waste basket" fire extinguishment tests, PBTFE proved effective in extinguishment. Comparison testing with other agents was not performed, however.

Preliminary toxicity testing was performed over a five week period, with PBTFE being fed to gold fish in water with techniques established for preliminary evaluation of other firefighting agents. (In this instance, gold fish were placed in 1.5 liters of water, in which PBTFE had been suspended in a matrix of fish food. No deleterious effects on the fish were noted. Based on analogies with other innocuous polymers (polystyrene, polyvinyl chloride, polyvinylidene chloride, etc.) formed

from mutagenic/carcinogenic/toxic monomers, it might be anticipated that toxic effects of the NVP polymeric agents might be equally benign. It is obvious, however, that much more complete toxicology studies need to be performed.

Our entire lot of PBTFE was then submitted for evaluation to Wright Laboratories for evaluation in engine nacelle fire suppression tests. We have to date been unable to ascertain the success of WPAFB tests for PBTFE.

B. Halogenated polyesters.

A number of brominated and fluorinated polyesters were examined as potential NVP agents. Some of these (in particular, those noted below) appeared to be quite attractive NVP candidates:

Poly(vinyl tribromoacetate)
Cellulose Tribromoacetate
Poly[1,4-(2,2,3,3-tetrabromo-1,4-butylene) oxalate]

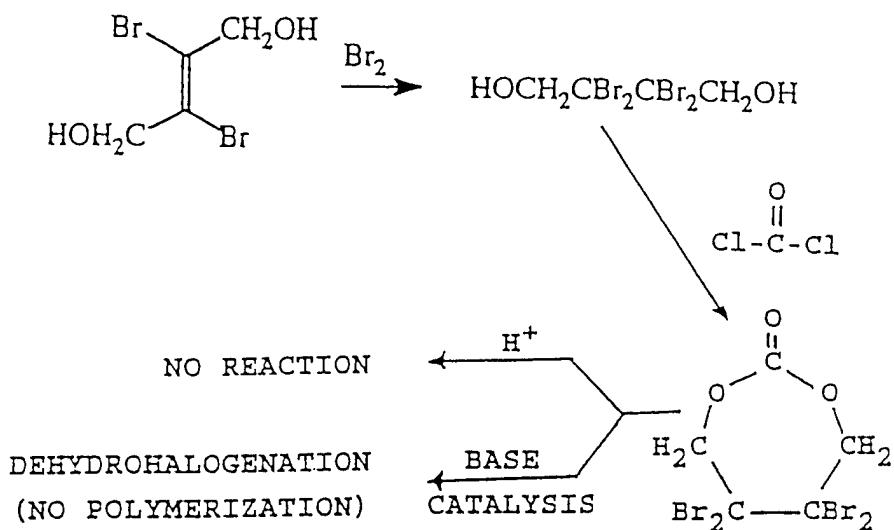
This sub-phase was predicated on the commercial availability of a number of polyhydroxy compounds, including cellulose, polyvinyl alcohol, and 2,3-dibromo-2-butene-1,4-diol; halogenated carboxylic acids (including bromo- and bromofluoro-substituted acetic acid); and polycarboxylating species such as phosgene, tetrafluorosuccinic acid, *et al.*

Polyesters derived from 2,2,3,3-tetrabromo-1,4-butanediol.

This diol was prepared by addition of bromine to the commercially available *trans*-2,3-dibromo-2-butene-1,4-diol.

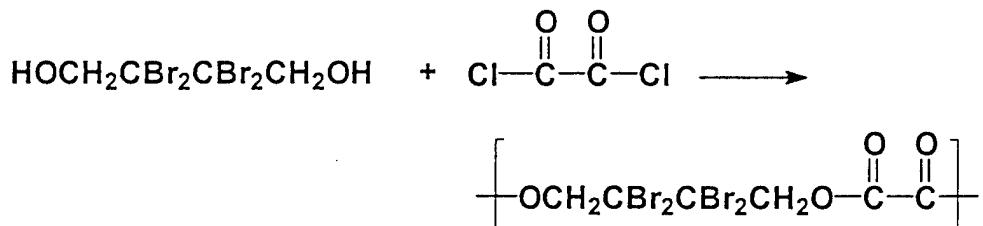
Attempts to form a polycarbonate:

Polymerization to form a polycarbonate was attempted using phosgene (with triphosgene as a phosgene precursor) with 2,2,3,3-tetrabromo-1,4-butanediol. As noted below, a cyclic seven-membered ring carbonate was readily formed instead of the desired poly(2,2,3,3-tetrabromo-1,4-butylene carbonate). Polymerization of this carbonate ester was attempted using acid catalysis (with no results) and base catalysis (resulting in extensive dehydrohalogenation). The entire synthetic procedures are summarized below:



Poly[1,4-(2,2,3,3,-tetrabromo-1,4-butylene)oxylate] formation:

The polyoxylate was prepared by condensation polymerization, using oxalyl chloride instead of phosgene, and with pyridine as a solvent and sink for evolved HCl. The analogous eight-membered ring was anticipated to be less favored than the seven-membered ring observed with the carbonate system; and indeed polymerization did occur.



Excellent pyrolytic degradation was noted in the TGA, with little or no charring observed. (See Figure 4.)

Sample: POLYOXALATE
Size: 11.1380 mg
Method: 10 °C/MIN
Comment: TG

TGA

File: C:POXOLATE.000
Operator: ARVINO
Run Date: 25-Apr-96 10:08

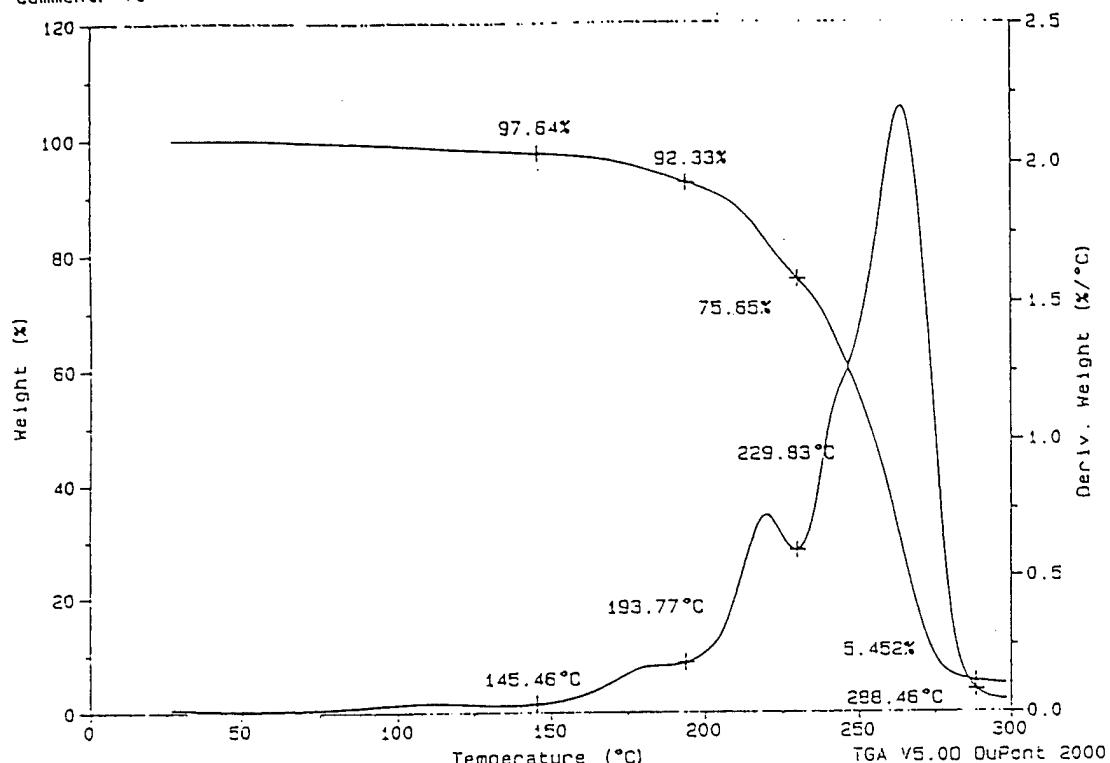
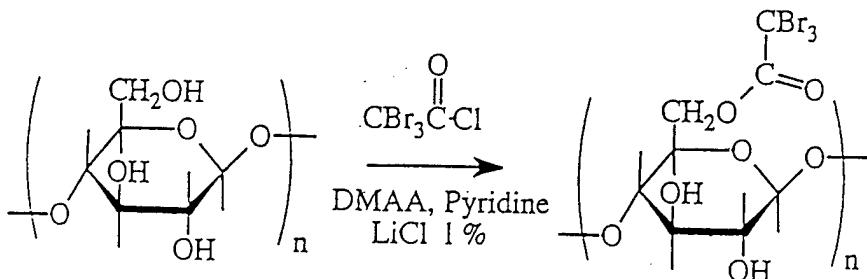


Figure 4. TGA of Poly[1,4-(2,2,3,3,tetrabromo-1,4-butylene)oxalate]

Cellulose Tribromacetate

This agent was prepared by acylation of cellulose in dimethylacetamide. The tribromoacetate moiety is quite bulky, and as a result the degree of substitution for this agent was only about 20%; the most likely point of substitution on the cellulose moiety would be at the #6 carbon, since this location poses the least steric hindrance of the three available hydroxy groups in each of the glucose components of the cellulose strand.



Degree of Substitution = 20%

Despite the low degree of substitution, excellent pyrolytic decomposition was seen in the TGA; see Figure 5. (The pyrolysis also resulted in some charring as a result of decomposition of the glucose carbohydrate moiety.)

Sample: CELLULOSE BROMOACETATE
 Size: 6.2300 mg
 Method: 20 °C/MIN
 Comment: UNDER NITROGEN

TGA

File: C:CBRAC.001
 Operator: ARVINO
 Run Date: 17-Apr-96 15:52

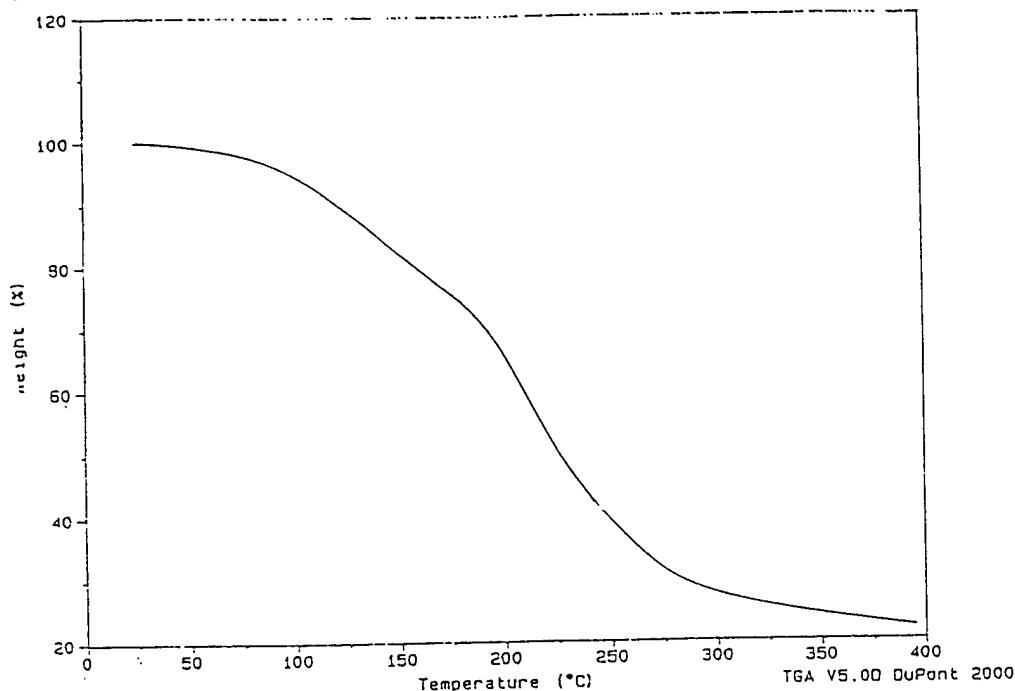
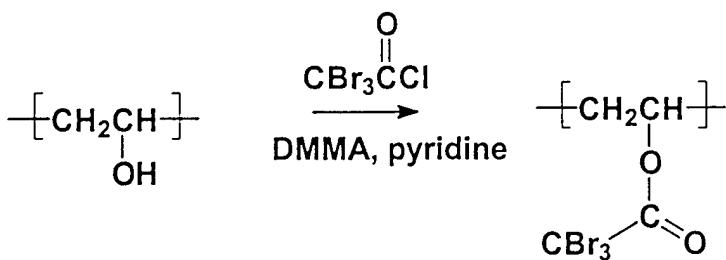


Figure 5. TGA of Cellulose Tribromacetate

Polvinyl Tribromoacetate

This agent was prepared by acylation of polyvinyl alcohol by tribromacetyl chloride in dimethylacetamide. Despite the steric requirements of the bulky tribromoacetate, the polyvinyl backbone is considerably more open to substitution than is the case for cellulose; accordingly, the degree of substitution for this agent was found to be in excess of 50%. It would perhaps be feasible to prepare this polymer in satisfactory yield by direct polymerization of the monomeric vinyl tribromoacetate, which should result in a very high degree of substitution.



Again, excellent pyrolytic decomposition was seen in the TGA; in this instance, very little charring or other residue was noted. (See Figure 6.)

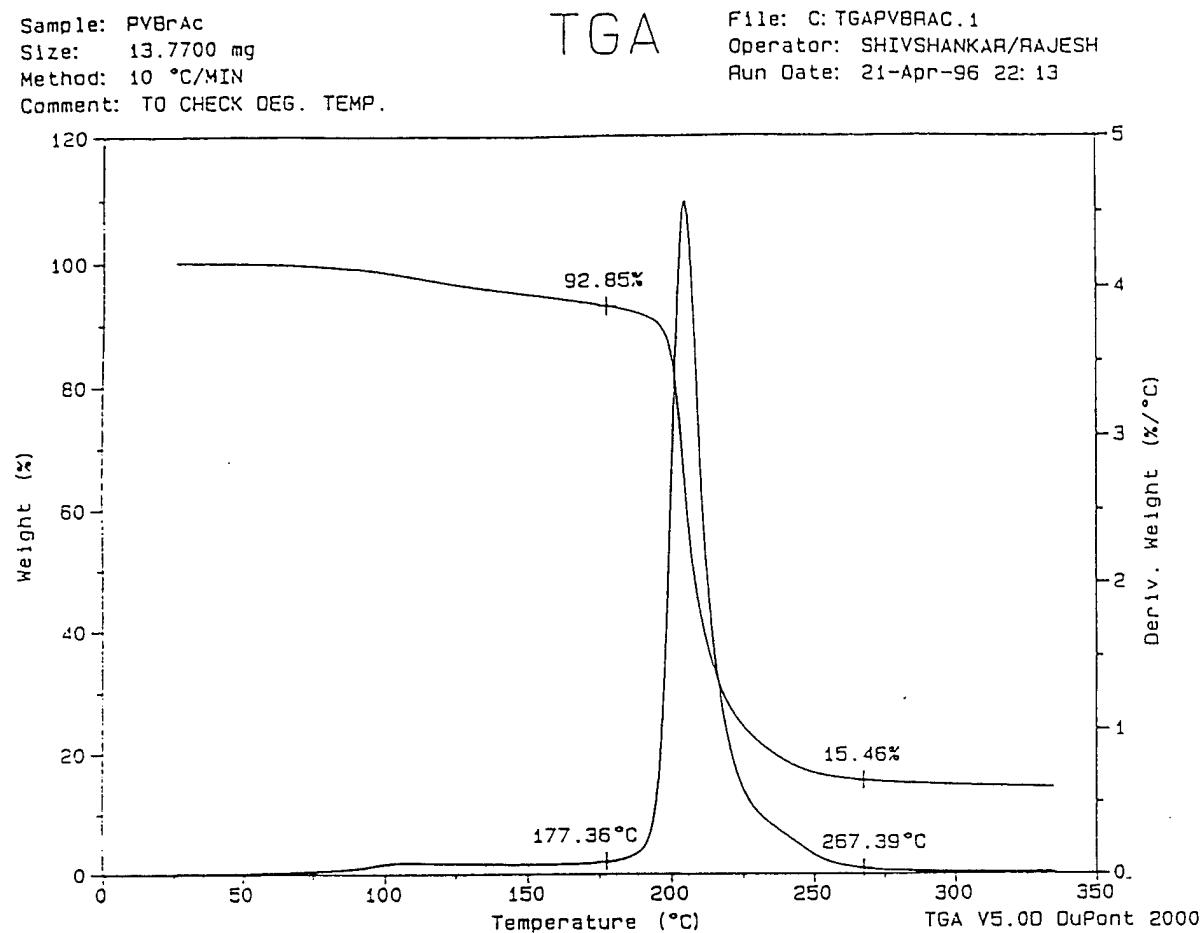
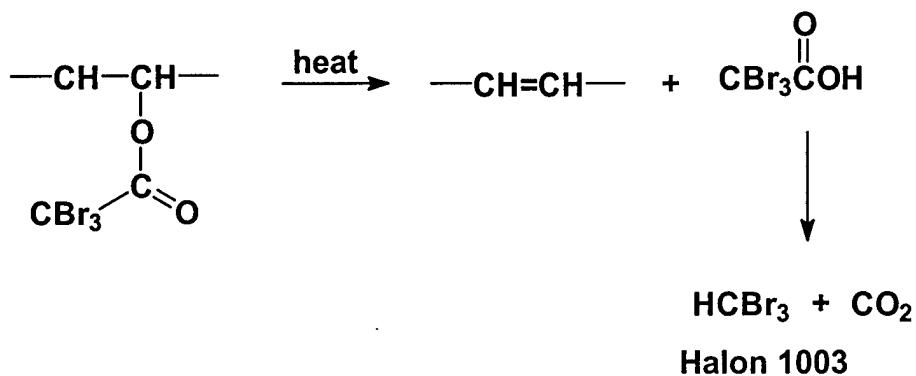


Figure 6. TGA of Polyvinyl Tribromoacetate

For both of these materials, excellent pyrolytic profiles were obtained in the TGA curves with little or no charring observed.

The expected mode of decomposition of the polyvinyltribromoacetate would give Halon 1003; the cellulose analog should behave similarly.



The pyrolysis of poly(1,4-(2,2,3,3-tetrabromo-1,4-butylene)oxalate) would be expected to produce brominated olefins and carbon dioxide, although we have not fully investigated the products of this reaction.

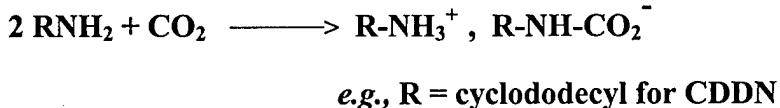
By using dibromofluoroacetyl chloride as the acylating agent, the resulting dibromofluoroacetyl group would be expected to produce CFBr_2H (Halon 1102), which has been shown to be an excellent HBFC extinguishing agent.

PHYSICAL MODIFICATION (GELATION) OF HIGH VOLATILITY HALONS

Physical modifications of existing high volatility Halons or alternatives were also being studied. These include gelation (using a variety of highly effective gelants to form relatively non-volatile formulations); or encapsulation under pressure in expandable polymeric microspheres for delivery to a fire.

A. Amine gelling agents.

Small amounts of cheap, low toxicity amines such as cyclododecylamine ("CDDN"), dehydroabietylamine ("Amine D"), and other commercially available amines dissolve easily, completely and quickly into Halon and similar halogenated extinguishing formulations. Upon addition of very small amounts of carbon dioxide, carbamate formation and gelation of the solution occur practically immediately:



(Small amounts of water facilitate the process.) The process is applicable to any Halon system, providing very greatly enhanced deliverability to a fire. Moreover, volatilities of the Halons are drastically reduced, thus practically eliminating any evaporation en route to the fire (during which time ungelled volatile Halons will

almost completely evaporate, requiring very large excess of agent in order to achieve adequate extinguishing concentration at the fire zone itself).

In a recent test with Halon 1211 (b.p. -2.5°C) a solution was prepared at -10°C with components as indicated below. After carbonation with 2 g of Dry Ice, gelation occurred upon warming to just above 0°C. After warming to 20°C and standing in an open beaker for another 10 minutes, and then subsequently for 24 hours, the compositions were determined to be as indicated below:

	INITIAL	10 MINUTES	24 HOURS
Halon 1211	40.0 g	21.0 g	16.0 g
CDDN	2.5 g	2.5 g	2.5 g
Nujol mineral oil	11.5 g	11.5 g	11.5 g
Water	1 g	1 g	1 g

(Naturally, ungelled Halon 1211 would have completely evaporated within a minute at 20°C.)

The gel is a thick grease, which can easily be projected long distances from a modified flamethrower as shown in Figure 7. Alternatively, the gelation process can be accomplished by introduction of the components into a fire hose and projected with a long distance stream with the gelled Halon held in the water, from the hose nozzle. On heating in a fire zone, the gelled Halon readily liberates the extinguishing agent. The spent mineral oil/CDDN residue would provide significant anti-corrosion attributes, readily removable by action of water, and for most POL considerations should not be considered a "dirty" residue problem.

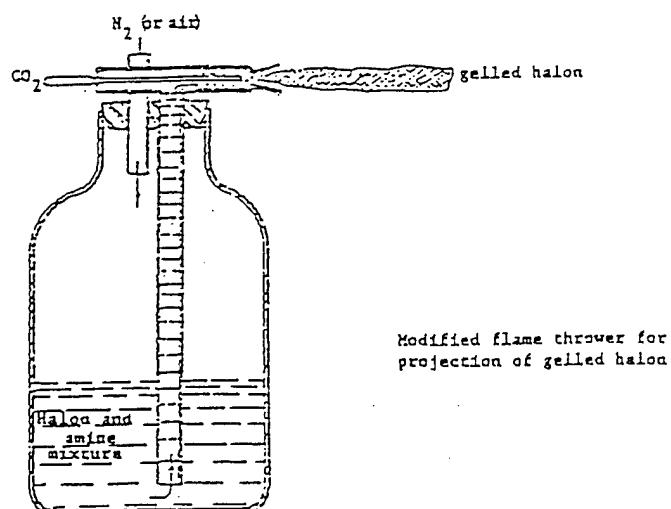


Figure 7. Modified flame thrower for projection of gelled Halon formulation.

B. Hydrophobic fumed silica gel formulations.

CAB-O-SIL™ and similar fumed silica gel formulations have the capability of absorbing significant amounts of volatile organics, including the Halons and similar halogenated extinguishing agents. On heating in a fire zone, the gelled Halon is readily liberated as the extinguishing agent. The spent silica gel would be readily removable by action of water, and for most POL considerations should not be considered a "dirty" residue problem. The silica gel would be considered as a "dirty" problem for engine fires, however. The silica gels should be efficient for lower volatility streaming agents, but probably would not be very effective for high volatility agents.

C. HYPOL™ (Hampshire Chem. Co.): Prepolymer Gels.

Hypol agents are hydrophilic urethanes which react readily with water to form gelled elastomeric products. (These materials have been used as dental foams and in other medical formulations; they are entirely non-toxic.) In the presence of volatile organics (e.g., Halons or similar volatile halogenated extinguishing agents) the gelled product is a foam containing the volatile gas.

In recent work by our group, both Halon 1211 and trifluoromethyl iodide were separately trapped in sufficiently high concentrations as to readily extinguish "wastebasket" fires when the gelled Hypol formulation was scattered over the fire.

Alternatively, the gelation process could have been accomplished by introduction of the components into a fire hose and projected with a long distance stream into the fire zone. Depending on the type of Hypol agent which would be used, the gelled formulation could be thrown as a stiff foam or as an adhesive mixture which would adhere to vertical structures to liberate the Halon in a three-dimensional matrix within the fire zone.

On heating in a fire zone, the gelled Halon readily liberates the extinguishing agent. The spent Hypol residue would be removable by action of water, and for most POL considerations should not be considered a "dirty" residue problem.

PROBLEM AREAS

From the standpoint of determination of fire extinguishing capabilities,₁ a good analog of the cup burner testing apparatus developed at NMERI and elsewhere is needed for bench scale evaluation of these solid NVP agents. In preliminary "waste basket" fire extinguishment tests, PBTTFE proved effective in extinguishment. This type of testing is highly subjective₁ however. (The monomeric bromotrifluoroethylene which was identified as being the sole product of cracking of PBTTFE was tested using the NMERI cup burner apparatus at Tyndall AFB, and was shown to be comparable in effectiveness to the Halons and for CF₃I.)

Pending successful development and completion of bench scale means of evaluation of NVP agents, and determination of non-toxic effects of these agents, large scale field tests could then be performed to establish the efficacy of any NVP agent system.

RECOMMENDATIONS FOR FUTURE WORK

Dendrimers. (See Reference 6.) Recently there have been many developments in the field of highly branched macromolecules. The initial developments pertained to dendrimers, which are rather expensive but highly defined macromolecules with unique chemical and physical properties. Typically, these have a complex architecture with a multitude of functional groups such as alcohol carboxylic acid, and similar moieties that can be further functionalized. Thus, hydroxyl groups can be esterified with carboxylating reagents; and, if the approach we utilized for attaching fluorobromoacyl groups, suitably substituted dendrimeric structures could be realized. A major advantage that would accrue would be the availability of many such groups within a single molecular entity. It would then be anticipated that a sudden and massive release of volatile Halon subunits would occur when suitably heated in a fire zone.

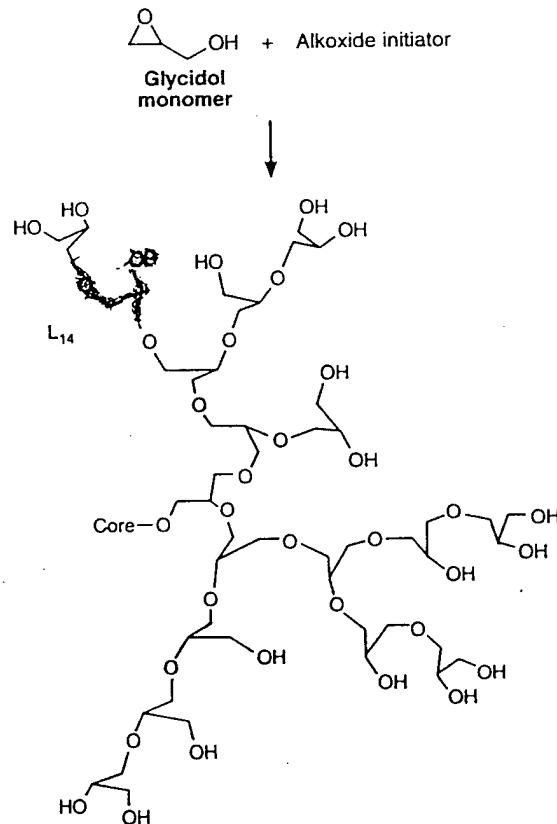


Figure 8. Hyperbranched polyglycerol, prepared in one step. (See Reference 6.)

Hyperbranched polymers derived from natural sources. (See Reference 6.) Even more recently, there has been reported use of naturally occurring polyfunctional materials such as glycerol, cellulose (as indeed our group innovated in this research), glycidol monomer, *et al.* in such functionalizations. (See Figure 8, above, in which the pendant polymer's hydroxyl groups, or the monomeric hydroxyl group can easily be esterified.)

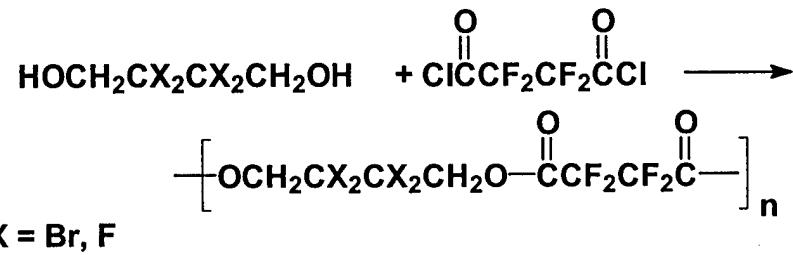
It is recommended that these approaches undergo further study toward synthesis of potentially useful NVP agents.

Gelation of high volatility Halon agents. Our work was able to demonstrate that the volatility of highly effective Halon agents can be substantially reduced by gelation. This concept maybe useful in terms of extending use of current agents in the Halon Bank.

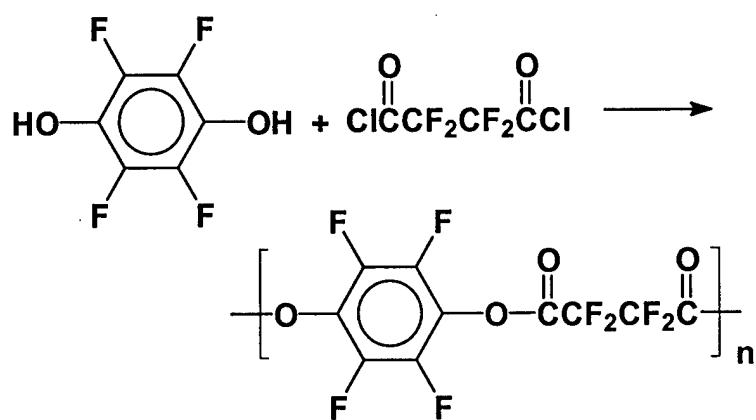
Further toxicity studies. Based on analogies with other innocuous polymers (polystyrene, polyvinyl chloride, polyvinylidene chloride, etc.) formed from mutagenic/carcinogenic/toxic monomers, it should be anticipated that toxic effects (for both human and marine animal considerations) of the NVP polymeric agents might be equally benign. It is obvious, however, that much more complete toxicology studies need to be performed.

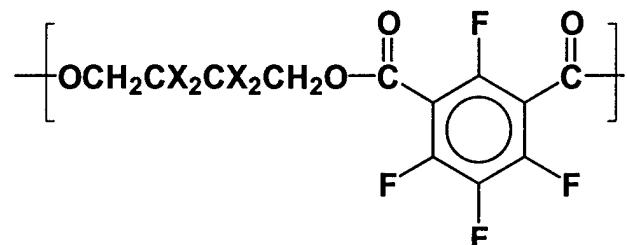
Field tests. Due to limited availability of the NVP agents we studied, and developing requirements for more toxicity tests than had originally been contemplated) we were unable to conduct meaningful field tests. These would be of interest in terms of comparing the results of lab tests (*e.g.*, cup burner tests) with actual field data.

The potential success of linear polymeric material with high halogen content has led to the current synthetic efforts which center around systems with fluorine substitution. Fluoro polymers have been used for a number of applications such as linings for valves, pipes, cable insulation as they do not support combustion. The commercially available 2,2,3,3-tetrafluorosuccinic acid could thus be was converted to the acid chloride for condensation polymerizations with both linear and flexible monomer units for syntheses of interesting NVP agents:

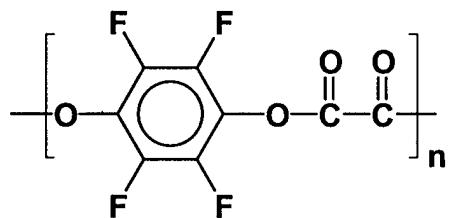
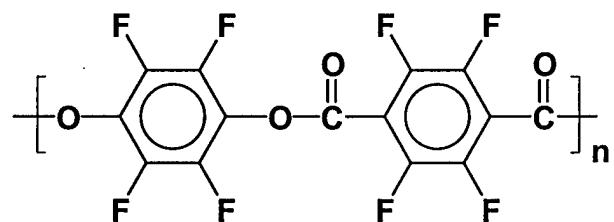
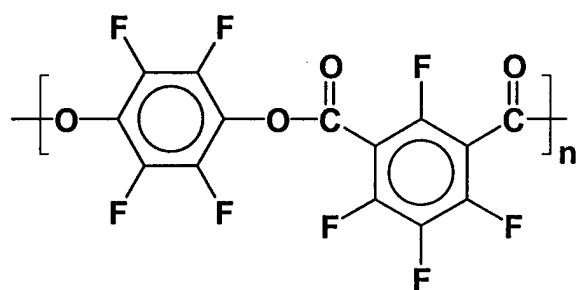
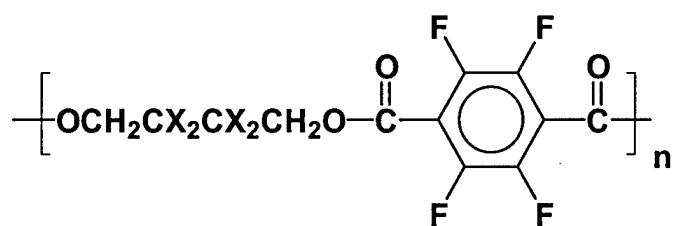


or with more rigid aromatic fluoro compounds:





X = Br, F



In addition to the polyesters, polyamides can also be prepared.

SIGNIFICANCE OF RESULTS

NVP agents have greatly reduced ODP, GWP and toxic vapor properties, and pose greatly reduced atmospheric emissions due to fire extinguishing operations or from accidental releases. Agent requirements for firefighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances. This improved agent system may be beneficial in terms of optimizing usage of Halon streaming agents in the Halon Bank. NVP agents can be incorporated into fire preventative paints and resins which will release Halon agents upon exposure to high heat.

PERSONNEL SUPPORTED

(All individuals except Mr. Floden were or are members of the Chemistry Department, University of Massachusetts at Lowell. Mr. Floden was associated with the Floden Consulting Group, Stillwell, Kansas.)

Faculty: William W. Bannister, Arthur C. Watterson

Postdoctoral Staff: Nagendra Kodali
Chang-Yuang Li
David W. McCarthy
Arvind Viswanathan

Consultants: John R. Floden, P.E.

Graduate Students: Alec Crawford
Steven Kumiega
Ruckyard Tirisirichai

Undergraduate Students: Eric Chen
John Patronick
Brian Tolan

PUBLICATIONS

(There have been no publications resulting from this project in the past year (except for the papers involving "Low Volatility Halon Fire Extinguishing Agents with Reduced Global Environmental Impacts" which have been presented at technical conferences. (See References 1-5.)

INTERACTIONS

Presentation of numerous papers involving "Low Volatility Halon Fire Extinguishing Agents with Reduced Global Environmental Impacts" have been presented at technical conferences. (See References 1-5.)

NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES

Based on the successful results of this group on this project, it is our understanding that other research groups (in particular with support from the National Institute of Standards and Technology) have extended these studies to include halogenated dendrimeric polymers as potential NVP agents. It is our further understanding that at least some of this extension work has had very successful results.

An (unauthorized) patent disclosure was submitted on this project work, with subsequent award of a U.S. patent (No.), by a consultant to this group (John R. Floden).

HONORS/AWARDS

There have been no honors or awards for this work in the past year.

REFERENCES (Note: Reference #6 has been added since the original submission of this report.)

1. W. W. Bannister, et. al. Proceedings of the Halon Options Technical Working Conference, Albuquerque, NM (1991); pp. 281-294.
2. W. W. Bannister, et. al. Proceedings of the Halon Options Technical Working Conference, Albuquerque, NM page (1992); pp. 126-136.
3. W. W. Bannister et al., Proceedings of the 1993 Intl. CFC and Halon Alternatives Options Conference, Washington, DC. (Oct. 20-22, 1993); pp. 761-766.
4. W. W. Bannister, et. al. Proceedings of the Halon Options Technical Working Conference, Albuquerque, NM (1994).
5. W. W. Bannister, et. al. Proceedings of the Halon Options Technical Working Conference, Albuquerque, NM (1994).
6. Freemantle, M. "Hyperbranched polymers May Rival Dendrimers". Chem. & Eng. News (September 6, 1999), pp. 37-39.

Acknowledgments

Appreciation is extended for the generous financial and technical support provided this group by the following:

**Air Force Office of Scientific Research
Directorate of Chemistry and Materials Science
Bolling AFB, D.C.
Dr. Frederick Hedberg and Dr. Walter Kozumbo**

**Air Force Wright Laboratories
Fire Protection Research Section (WL/FIVCF)
Tyndall AFB, Florida
Mr. Richard Vickers, Chief**

**New Mexico Engineering Research Institute
Center for Global Environmental Technologies
University of New Mexico
Albuquerque, New Mexico
Dr. Robert Tapscott, Director**